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SOME FACTORS AFFECTING THE COOKING
OF DHOLL (*CAJANUS INDICUS*)

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PREFACE.

THE experiments detailed in the following pages have been made under conditions obtaining in South India. It is possible that the immediate results vary somewhat under other conditions: but the broad conclusions drawn therefrom, we believe, will hold good generally.

We beg to acknowledge our indebtedness to Dr. W. H. Harrison, Government Agricultural Chemist, Madras, not only for the facilities kindly afforded us for conducting the experiments but also for the very kind advice and help so willingly given in spite of much personal inconvenience to himself.

COIMBATORE,
November, 1915.

B. V. N.
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Red gram or Pigeon pea (*Cajanus indicus*) is extensively cultivated in India as a food-crop and is regarded as third in rank of importance among the leguminous seeds.¹ Unlike peas and some other beans which are cooked green, the red gram is cut after it is ripe and allowed to dry in the sun. The seeds are afterwards broken into dhol, the husk removed, and then cooked.

In Southern India the gram seeds, after drying, are first mixed with red earth and water and allowed to steep for one night and then dried in the sun before being broken into dhol. For use as food this dhol is boiled in water and afterwards eaten in conjunction with other foodstuffs such as rice and vegetables. In the South Indian dietary it is this pulse which is chiefly depended upon by vegetarians to increase the nitrogenous content of rice-foods.

The cooking qualities of different dholls vary considerably, some requiring long continued boiling to reach the desired stage whilst others cook quickly and the object of the purchaser is naturally to acquire the latter type. Apart from the cooking qualities of different dhol varieties it is a point of general belief that the quality of the water used for boiling has a considerable effect upon the rate of cooking and it is mainly with this aspect of the case that the experiments detailed in the following pages are concerned.

¹ Watt. *Commercial Products of India*, 1908.

In determining the various factors which affect the rate of cooking of dholl it is of course impossible to examine all possibilities and this enquiry has been limited to the following :—

- I. The effect of the composition of the water upon the rate of cooking.
- II. (a). The influence of the fat content on the rate of cooking.
(b). Differences in the rates of cooking due to variety.
(c). Differences in the rates of cooking due to methods of preparing the dholl.
- III. The influence of various salts on the liquefaction of starch.

PART I.

THE EFFECT OF THE COMPOSITION OF THE WATER UPON THE RATE OF COOKING.

Before undertaking a detailed enquiry upon the effect of the different salts usually found in South Indian waters upon the rate of cooking, it was deemed desirable to ascertain whether or not the rate of cooking varied with waters of different composition. For this purpose water of very different quality derived from five sources was used. The composition of these waters is shown below :—

TABLE I

Showing the composition of the various waters taken for experiment.

(Parts per 100,000)

Name of well	CaCO ₃	MgCO ₃	Na ₂ CO ₃	CaSO ₄	MgSO ₄	Na ₂ SO ₄	CaCl ₂	MgCl ₂	NaCl	Total solids
Joseph's well	12.49	6.06	1.46	1.82	6.35	38.0
No. 57 well	41.04	0.82	48.10	4.84	135.19	264.0
College well	33.02	4.22	29.47	4.72	89.03	166.0
Dwaraka well, Madras	15.01	8.41	56.23	41.97	285.62	560.0
Kaladindy Ravu drain water, Kistna	12.01	59.00	66.00	137.00	928.00	1225.0

In testing the effect of these different waters the procedure followed was of a purely empirical character. The dholi used was obtained from the Central Farm, Coimbatore, and was carefully sorted out so as to exclude all bad or damaged ones, and in addition was passed through a 4 m.m. sieve so as to obtain a sample of approximately uniform size. Twenty grammes were added to 250 c.c. of water contained in a beaker and the whole boiled until the cooking was judged to be complete. During this process care was taken to maintain the water at the same constant level and for the sake of comparison an experiment was carried out with distilled water. The dholi was judged to be properly cooked when it could be easily crushed between the fingers.

The times taken to cook the dholi by the different waters were as follow :—

Distilled water	37 minutes.
Joseph's well	37 „
College well	48 „
No. 57 well	50 „
Dwaraka well	over	60 „
Kaladindy drain water	75 „

There can, therefore, be no doubt that the presence of dissolved salts in water materially affects the time taken to cook the dholi.

In South India it is a common practice to add a pinch of sodium bicarbonate to the water as this is found to materially accelerate the rate of cooking. Consequently the above experiment was repeated after adding a pinch of this substance to the several waters. The times taken were then as follow :—

Distilled water	20 minutes.
Joseph's well	20 „
College well	23 „
Dwaraka well	40 „
Kaladindy drain	50 „

It becomes evident, then, that the presence of an alkaline substance in the water materially accelerates the rate of cooking.

The rate of cooking of dholi appears to depend upon two factors, namely, the amount and the kind of dissolved substances present. A series of experiments was carried out with the object of determining the effect of different classes of salts upon the rate of cooking. These tests were carried out in beakers as described above. The results are given in Table II.

TABLE II

Showing the rate of cooking of dholl in different solutions of varying strengths in minutes.

Strength of solution in parts per 100,000	10	20	50
Distilled water	...	17	...
MgCl ₂	20	23	24
NaCl	18	24	24
CaCl ₂	24	32	46
Na ₂ CO ₃	18	18	16

One curious result obtained was the retarding action of CaCO₃ suspended in distilled water. With amounts equal to 10, 20, 50 and 100 parts per 100,000 the corresponding times were 18, 21, 35 and over 86 minutes respectively.

These results bear out the conclusion that the rate of cooking with neutral salts varies with the kind and the amounts used, the effect being a retardation, whereas, in the case of alkaline salts the rate of cooking is accelerated, the acceleration increasing with the concentration.

The foregoing experiments were only of a preliminary nature and were of a rough and ready type, so that they could only be looked upon as giving approximate results. In order to obtain more accurate data, particularly with reference to the mode of action of the various salts, some other method of experiment was desirable.

After a number of different procedures had been tried the following was selected as giving the most accurate results. During the process of cooking, a certain amount of disintegration of the dholl takes place resulting in the solution of amylaceous material. The basis of comparison taken in the following experiments was the amount of amylaceous matter passing into solution when the dholl was boiled with different solutions for a fixed time. In carrying out these determinations, 250 c.c. of distilled water or of an aqueous solution were introduced into a litre flask closed with a cork through which passed a

reflux condenser. The liquid was raised to the boiling point and maintained there whilst the condenser served to keep the volume constant. When the rate of boiling was quite uniform the cork was momentarily removed and ten grammes of dhol added and the boiling continued for sixteen minutes, a period of time which experience showed was long enough to give a differentiation between the degrees of cooking with the various solutions and to give comparable results with duplicates.

At the end of this period the flask was rapidly cooled and the contents were then filtered through fine muslin so as to remove the residual dhol. 100 c.c. of the filtrate were transferred to an Erlenmeyer flask, 20 c.c. of pure HCl of sp. gr. 1.125 were added and boiled for one hour so as to hydrolyse the amylaceous matter present. As in the previous case, a reflux condenser served to maintain the volume constant. The flask was then rapidly cooled and after making slightly alkaline with caustic soda 20 c.c. of alumina cream were mixed with the contents. The volume was made up to 250 c.c. with distilled water and the liquid filtered. The reducing sugar present was determined volumetrically with Fehling's solution and the result calculated as starch.

In the same way by determining the amount of nitrogen in the residual dhol it is possible to estimate the proteid matter which had passed into solution and thus determine the effect of the solutions on the proteids of the grain. Thus the complete series of determinations for a single experiment can be made to cover the following points :—

1. Weight of dhol taken as dry matter.
2. Weight of dry matter left after boiling.
3. Weight of proteids in original dhol.
4. Weight of proteids in dhol after boiling.
5. Weight of starch passing into solution.

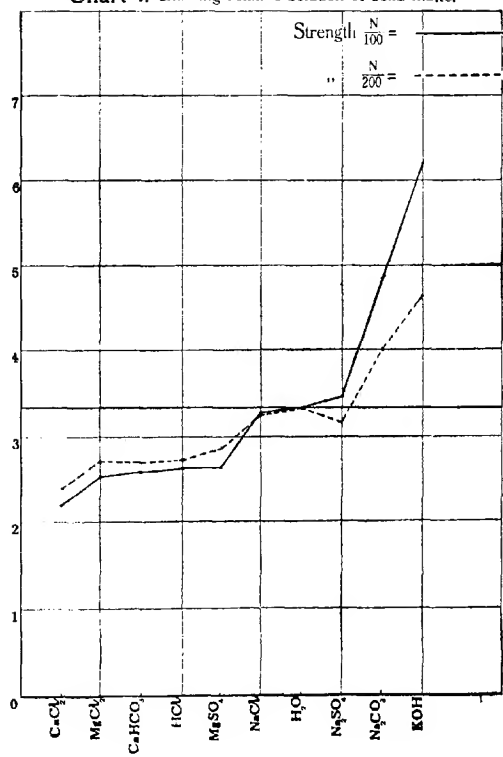
The difference between 1 and 2 gives the amount of dry matter removed during the process of boiling and that between 3 and 4 the amount of proteids passing into solution, so that it is possible to compare the action of different salts on both the starch and proteids present.

The solutions used were of strengths $\frac{N}{100}$ and $\frac{N}{200}$. The results obtained are given in Table III.

TABLE III
Showing comparative action of different salts on the cooking of dholl.

Solutions	N 100					N 200				
	Residue after boiling	Matter removed by boiling	Total	Proteid matter in unboiled dholl	Proteid matter in residual dholl	Proteid matter removed by boiling	Total	Proteid matter in unboiled dholl	Proteid matter in residual dholl	Proteid matter removed by boiling
Water ...	6.67	3.33	10.00	2.33	1.71	0.62	10.00	2.33	1.71	0.62
Sodium chloride	6.72	3.28	10.00	2.33	1.74	0.59	10.00	2.33	1.68	0.63
Magnesium chloride	7.46	2.54	10.00	2.33	1.89	0.14	10.00	2.33	1.85	0.18
Calcium chloride	7.80	2.20	10.00	2.33	1.91	0.39	10.00	2.33	1.90	0.43
Calcium hydrogen carbonate	7.39	2.61	10.00	2.33	1.79	0.54	10.00	2.33	1.76	0.57
Sodium carbonate	5.19	4.81	10.00	2.33	1.27	1.06	10.00	2.33	1.53	0.81
Caustic potash	3.80	6.20	10.00	2.33	0.86	1.47	10.00	2.33	1.32	1.01
Hydrochloric acid	7.37	2.63	10.00	2.33	1.90	0.43	10.00	2.33	1.82	0.51
Sodium sulphate	6.51	3.49	10.00	2.33	1.59	0.74	10.00	2.33	1.67	0.66
Magnesium sulphate	7.34	2.66	10.00	2.33	1.86	0.47	10.00	2.33	1.75	0.58

Chart I. showing relative solution of solid matter



These results bear out the previous conclusion that the rate of cooking is affected by the character and the amount of salt present. This is clearly shown in charts I, II and III where the values obtained are plotted out in the form of graphs.

It will be seen that certain salts retard the rate of cooking as compared with distilled water, whereas others cause an acceleration. This effect is evidently due to the influence the salts exert in modifying the solvent action of the water. Those salts which cause retardation are those which decrease the solvent action of the water and *vice versa*.

As would be expected on this basis, the general effect of increasing concentration in the case of those substances which cause retardation is to increase the amount of retardation, whereas those which bring about an acceleration do the reverse. As a general rule, chlorides, sulphates and carbonates cause retardation, whereas alkalis and alkaline carbonates bring about an acceleration. HCl, curiously enough, acts as a retarding agent. The broad conclusion to be drawn is that hard waters retard the rate of cooking in proportion to the amount of salts they contain and that alkaline waters accelerate it.

The mode of action of the substances studied is not, however, merely due to a solution of the dholl substance quite independent of its constitution, but is partially due to a selective solvent action with respect to the proteids and starch.

This is clearly shown by a comparison of the relative amounts of starch and proteid which go into solution during the boiling process.

TABLE IV
Showing $\frac{\text{Starch}}{\text{Proteid}}$ ratio in the solutions.

Solutions	N. 100	N. 200
Na ₂ CO ₃ ...	0.73	0.88
KOH ...	0.77	1.02
CaHCO ₃ ...	0.91	0.88
Na ₂ SO ₄ ...	0.94	1.03
NaCl ...	1.02	0.97
MgSO ₄ ...	1.09	0.93
CaCl ₂ ...	1.10	1.07
H ₂ O ...	1.12	1.12
MgCl ₂ ...	1.14	1.10
HCl ...	1.37	1.06

With N. 100 strengths water has a ratio of 1.12 and this is closely approximated only by CaCl₂ and MgCl₂ and NaCl and MgSO₄ do not vary greatly

from this figure, showing that the solvent action in each case has been of a very similar nature. HCl, however, gives a much higher ratio, showing that the action of this substance is to increase the proportion of starch dissolved. On the other hand, KOH and Na_2CO_3 have greatly increased the proportion of proteid matter going into solution and the same holds good to a lesser degree for CaHCO_3 and Na_2SO_4 .

These relations account for the discrepancies shown by HCl in Chart III.

The fact that the substances which have the greatest effect in accelerating the rate of cooking are those which exert a proportionately greater solvent action on the proteids than on the starch leads to the general conclusion that it is the rate at which the proteid goes into solution which is the determining factor and that substances which greatly accelerate this rate also accelerate the rate of cooking and *vice versa*. This view is strengthened by the fact that the substances which retard the rate of cooking most are substances which are precipitants for many proteids.

With the weaker strengths of N 200 the various ratios more nearly approximate to that of water, so that the relationships brought out above are not so marked. Nevertheless, they offer a general support to the view expressed.

The conclusions arrived at in this portion of the investigation may be summarized as follow :—

1. Dissolved salts, such as are found in natural waters, exert a marked influence on the time taken to cook dholl.
2. Calcium and magnesium salts and the chlorides of hydrogen and sodium exert a strong retarding effect, whereas alkalis and alkaline carbonates have the reverse action.
3. Whether the action exerted by any salt is a retardation or an acceleration, the effect is approximately proportionate to the concentration, *i.e.*, the harder the water, the slower is the rate of cooking.
4. That the addition of sodium bicarbonate or sodium carbonate to a hard water materially hastens the cooking.
5. The rate of cooking of dholl is approximately proportionate to the rate of solution of the dholl substance, *i.e.*, to the rate of solution of the proteid and starch.
6. The proportion of proteid to starch dissolved is not constant but varies with different solutions. Alkalis and alkaline carbonates

dissolve a greater proportion of proteid than starch as compared with pure water whereas hydrochloric acid dissolves a greater proportion of starch. In addition, alkalis and alkaline carbonates greatly accelerate the rate of cooking.

7. The rate of solution of the proteid appears to be the factor which mainly controls the rate of cooking.

PART II.

MISCELLANEOUS OBSERVATIONS RELATING TO THE COOKING OF DHOLL.

(a). *The influence of the fat content.*

In the previous section the influence of the various salts on the rates of solution of the proteid and starch was mainly considered. But there remains the possibility that the accelerators of the type of Na_2CO_3 and KOH act by saponifying the fat of the food stuff.

In order to test this point a sample of dholl was extracted for 15 days with successive quantities of ether. It was then air dried and boiling tests with distilled water were made in comparison with untreated dholl. The extraction removed 72 % of the fat originally present. The results obtained were as follow :—

Starch extracted per 100 grm. of dholl.		
	A	B
Extracted dholl	5.85	6.50
Unextracted dholl	6.25	6.60

It is evident that the removal of the fat has, if at all, only a very slight effect on the rate of cooking and that this effect is one of retardation.

It must therefore be concluded that the fat content of dholl plays a very unimportant part with regard to the rate of cooking.

(b). *The cooking rates of different dholls.*

It has been previously mentioned as a matter of common observation that dholls from different localities vary considerably in their rates of cooking and it was thought desirable to test this point by the methods adopted by us. A number of dholls from diverse localities were obtained and their several rates of cooking were determined by boiling a given weight with distilled water

for a fixed period as previously described and estimating the amount of amylaceous matter passing into solution.

TABLE V
Showing rates of cooking of various dholls.

A			B		
Source	Starch extracted per 100 gm.		Source	Starch extracted per 100 gm.	
Vallam ...	5.55		Coimbatore ...	6.41	
Mayavaram ...	5.93		Vizagapatam ...	6.50	
Karur ...	6.49		Godavari (In- terior) ...	6.75	
Panruti ...	6.76		Panruti ...	6.97	
Pallapalayam ...	6.92		Coconada ...	7.00	
Gulbarga, pale ...	7.00				
Gulbarga, red ...	7.17				

The figures bear out the common observation that different dholls vary in their rates of cooking.

The dholls under A were purchased as such and no information could be obtained with regard to the method of their preparation. This, as will be seen later, has some influence on the rate of cooking and the differences noticed are possibly partly due to differences in treatment as well. The figures under B refer to dholls prepared from gram with no preliminary treatment.

(c). *On the methods of preparing the dholl from the whole grain.*

The dholl as used for purposes of cooking is usually prepared by mixing the grain with water and red earth to a pasty mass and allowing the heaped up mass to remain in that condition for a certain number of hours after which it is spread out and sun-dried. It is then freed from the red earth, husked and the cotyledons separated, the latter forming the dholl. It is commonly believed that the duration of this soaking process is an important factor in determining the cooking qualities of the dholl and at the same time some importance is attached to the quality of water used in this process.

This treatment, no doubt, produces incipient germination and thus affects, to some extent, the character of the constituents and the rate of cooking. It is also conceivable, in view of our results, that the quality of the water used would also have some effect. To test these points red gram as obtained from the field at the time of harvesting was subjected to the usual

treatment with red earth and distilled water for varying periods of time and the rate of cooking of the products compared with an untreated sample. The results obtained are as follow :—

Treatment	Starch extracted per 100 gm.
Untreated	6.71
Treated for 8 hours	6.15
.. 16 hours	6.10
.. 24 hours	6.51

It is evident that this practice is not justified, for it has led in all cases to a distinct retardation in the rate of cooking.

The effect of salts present in the water was contrasted in a similar manner with the following results :—

Treatment	Starch extracted per 100 gm.
Soaked in distilled water for 16 hours	6.59
Soaked in N 100 CaCl_2 solution	6.52
.. N/100 Na_2CO_3 solution	6.84

It is evident that the action of CaCl_2 is to retard the rate of cooking, whereas Na_2CO_3 accelerates it, so that the use of alkaline waters or the addition of sodium carbonate to the water used would be beneficial.

Further soaking in distilled water gives a materially slower cooking product than that given by absolutely untreated dholl and in fact, a sample soaked for 72 hours only yielded 5.76 gm. starch per 100 gm. dholl. This would point to the conclusion that the soaking of the seeds leads to lower the rate of cooking unless in solutions having an alkaline reaction.

In the same way soaking with red earth and N 100 Na_2CO_3 solution yielded a product giving 6.88 gm. of starch per 100 gm. of seeds as against the value of 6.10 when only red earth and distilled water were used.

It may, therefore, be concluded that the treatment with red earth has no merit in inducing a quicker rate of cooking unless the water used is of an alkaline nature. The use of Na_2CO_3 solution for this purpose can therefore be recommended.

Although the treatment with red earth does not improve the cooking qualities of the dholl, yet such a treatment permits the gram to be broken and

husked easier than either untreated gram or soaked grain and at the same time the dholl produced possesses a better colour. From this point of view this peculiar treatment receives justification.

The presence of amylolytic enzymes has been detected both in treated and untreated gram and no doubt the activity of these substances has an important bearing upon the cooking qualities of the products. In the extreme case where the gram was soaked for 72 hours very low cooking values were obtained. In this case the young sprouts were about an inch long and during the preparation of the dholl were broken off and lost. The dholl itself consisted very largely of hollow cotyledons showing that a large proportion of their substance had been transformed and translocated and the low cooking value of the residue is, therefore, no doubt, due to a corresponding increase in the proportion of cellulose and mineral matter.

The conclusions arrived at in this part of the investigation may be summarized as follow :—

1. The fat content of dholl plays a very unimportant part with regard to the rate of cooking.
2. Dholls of different localities have varying rates of cooking.
3. The practice of treating gram with red earth and water has a distinct retarding influence on the rate of cooking when compared with the untreated one, yet this treatment is advantageous in that it allows the gram to be broken and husked easier.
4. The use of hard waters along with red earth retards the rate of cooking of dholl while alkaline waters accelerate it, so that the use of waters which are alkaline in reaction or the addition of sodium carbonate to the water used would be beneficial.

PART III.

THE INFLUENCE OF VARIOUS SALTS ON THE LIQUEFACTION OF STARCH.

In the preceding sections it has been shown that different salts exert varying effects upon the rate of solution of the substance of red gram seeds and that this is accompanied by a similar variation in the rates of solution of the starch and proteid present. It seemed therefore of interest to determine the influence of these salts upon the rate of liquefaction of pure starch.

It is well known that solutions of the caustic alkalis KOH and NaOH convert starch into a paste even in the cold and that acids slowly dissolve it.

Regarding the influence of certain salts on the conversion of starch into paste Payen¹ in 1878 observed that cold saturated or half saturated solutions of KBr or NaBr convert starch into a paste but that other salts such as KCl have no such effect. He further states "starch possesses the property of combining with bases. Upon mixing together a solution of NaOH and water containing starch suspended in it a transparent colourless jelly is formed after a short time which is a compound of NaOH and starch. If this jelly is mixed with a 7% aqueous solution of CaCl_2 a double decomposition takes place and a thick white insoluble mass is formed which is a compound of starch and lime, NaCl being in solution. A series of compounds with starch as basis may be similarly formed."

Later, Asboth² confirmed these observations and Wolff and Fernbach³ showed that carbonates of calcium, magnesium and potassium caused a considerable increase in the viscosity of starch pastes. The latter authors in a still later contribution⁴ on the influence of some mineral substances on the liquefaction of starch state that experiments with starch previously washed until nearly free from calcium and magnesium show that NH_3 , Na_2CO_3 , MgCO_3 and CaCO_3 have about an equal effect whilst Al_2O_3 is without action.

None of these observations, however, throw any light upon the influence of many of the salts found in natural waters upon the rate of liquefaction of starch, and in view of the effect of such substances upon the rate of cooking of dholi it was deemed advisable to make an investigation on the subject.

Rice starch purchased as pure and passed through a 100 mesh sieve was used in these experiments. As it was impossible to make comparisons at a temperature of 100°C . as in the case of dholi, a temperature of 70°C . was adopted after a series of preliminary observations had been made.

All the solutions used except that of CaCO_3 were of N/10 concentration. In the case of CaCO_3 it was added in the solid state to the distilled water in such an amount as would have corresponded to a N/10 strength if it had been actually in a state of solution.

¹ Payen. *Industrial Chemistry*, 1878.

² *Repert. Analyt. Chemie.* 1887, 7, 299.

Compt. Rend. 1905, 140, 1403—1406.

Compt. Rend. 1906, 143, 363—365.

In carrying out these experiments one gramme of starch was added to 50 c.c. of the solution tested and the whole maintained at a temperature of 70°C. in a thermostat for one hour, being constantly stirred the whole time. At the end of this period the liquid was cooled and, if the nature of the solution demanded it, made neutral. 15 c.c. of a malt extract were then added and the saccharification allowed to proceed for two hours at 30°C. The liquid was then made up to 100 c.c. and filtered with kaolin and 50 c.c. of this filtrate was hydrolysed with HCl, cooled, made faintly alkaline with NaOH and the glucose determined with Fehling's solution. After correcting for the amount of reducing material contained in the malt extract, the result was calculated back to starch.

Warth and Darabsett¹ have shown that at 30°C. malt extract does not act on ungelatinised starch and this observation is confirmed by our own experiments. The results may then be taken as representing the amount of starch liquefied under the action of the solution experimented with.

A number of separate series of experiments were carried out, each series being done under uniform conditions and the average of these is as tabulated below :—

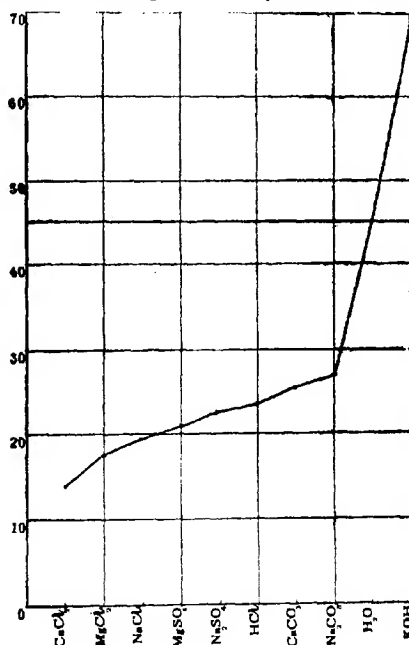
TABLE VI

Showing rate of liquefaction of starch by different N/10 solutions at 70°C.

Solution	% Starch liquefied
Potassium hydrate	67.51
Water	44.91
Sodium carbonate	26.62
Calcium carbonate	25.04
Hydrochloric acid	23.00
Sodium sulphate	22.06
Magnesium sulphate	20.40
Sodium chloride	19.00
Magnesium chloride	17.14
Calcium chloride	13.50

¹ *Memoirs, Dept. Agri. India, Chem. Ser.*, vol. III, no. 5.

Chart IV. showing relative liquefaction of Starch



The results are plotted out on Chart No. IV, where it will be seen that with the exception of KOH all the compounds experimented with give lower rates of liquefaction than distilled water. Na_2SO_4 and Na_2CO_3 which were found to accelerate the rate of cooking of dholi show a retardation with regard to the rate of liquefaction of starch and this fact strengthens considerably the conclusion previously advanced, that the effect of dissolved substances on the rate of solution of the proteid in dholi is the determining factor affecting the rate of cooking. Attention, too, has been already drawn to the fact that those substances which are used as precipitants for many proteids are exactly those which reduce the rate of cooking.

COIMBATORE,

November, 1915.

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